Molecular Packing Modes of Acyl Halides.
V. The Crystal and Molecular Structure of Adamantane-1,3-dicarbonyl Chloride

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Adamantane-1,3-dicarbonyl chloride (ACl), $C_{12}H_{14}Cl_2O_2$, crystallizes in space group *Pnma* with $a = 14.9761$ (12), $b = 6.8168$ (7), $c = 11.5207$ (6) Å, $Z = 4$. Four sets of refinements were carried out, differing in the treatment of weak reflections. The differences in the parameters adjusted in these four sets were smaller than their e.s.d.'s. Variations in R_w were small (0.06 to 0.075) compared to the differences in R (0.04 to 0.17). The isolated molecule possesses *mm2* symmetry. However, only the mirror plane which contains the two carbonyl chloride groups is retained in the crystal. The molecules are held together by nearly antiparallel $C^+=O^-$ dipole–dipole interactions (C$\cdots$O distances of 3.49 and 3.55 Å), and by Cl$\cdots$Cl contacts of 3.58 Å. No short Cl$\cdots$O contacts are present. The mean bond lengths and bond scatter of the CCOCl group are C–C 1.516 (1), C=O 1.175 (2) and C–Cl 1.800 (9) Å.

Introduction

Adamantane-1,3-dicarbonyl chloride (ACl) was chosen to study the geometry of the COCl group when it is attached to an sp^3 C atom, and to analyse the conformation and packing of a carbonyl halide bonded to a relatively large and rigid residue.

Experimental

Crystals of ACl grown by sublimation are colourless domes showing the {011} and {201} forms. To avoid contact with moisture they were sealed in lithium borate capillaries.

Cell constants were determined by least squares from 22 high-order ($20 < \theta < 30°$) reflections measured on a Siemens diffractometer with Mo $K\alpha$ radiation.

Crystal data

Adamantane-1,3-dicarbonyl chloride, $C_{12}H_{14}Cl_2O_2$, $M_r = 261.16$, m.p. 90°C, orthorhombic, $a = 14.9761$ (12), $b = 6.8168$ (7), $c = 11.5207$ (6) Å, $U = 1176.1$ (3) Å^3, $Z = 4$, $D_c = 1.545$ g cm^{-3}, $F(000) = 544$, μ(Mo $K\alpha$) = 5.34 cm^{-1}. Space group *Pnma* or *Pn2₁a* from systematic absences: $0kl$ for $k + l$ odd, $hk0$ for h odd; *Pnma* proved to be correct by the analysis.

Data-collection procedure

A crystal [0.19, 0.19, 0.36 and 0.34 mm bounded by the faces (011), (0$\bar{1}$1), (201) and (20$\bar{1}$)] was mounted along **a*** on an automatic Siemens diffractometer controlled by an IBM 1800 computer. 3156 reflections (sin $\theta/\lambda < 0.66$ Å^{-1}, one quadrant of the reciprocal sphere) were measured by the moving-crystal moving-counter technique with balanced Zr and Y filters. Scan ranges varied from 0.6 to 1.1°; time of measurement was 0.6 s (0.2 s for background) per 0.01° step interval. Lorentz and polarization as well as absorption (Coppens, Leiserowitz & Rabinovich, 1965) corrections were applied; transmission factors calculated with a Gaussian grid of 216 points varied from 0.892 to 0.923.

The data were averaged to yield 1544 independent reflections including 510 weak reflections for which $F_o^2 < \sigma(F_o^2)$; the agreement between symmetry-equivalent reflections is 0.033.

Structure determination

Intensity statistics based on the second and third moment tests (Foster & Hargreaves, 1963) as well as the $N(z)$ test (Howells, Phillips & Rogers, 1950) and the E-value statistics (Karle, Dragonnette & Brenner, 1965) favoured the centrosymmetric space group *Pnma*. The structure was solved by the symbolic addition method (Cochran & Woolfson, 1955; Karle & Karle, 1966). An E map based on 175 reflections with $E > 1.6$ revealed all the non-hydrogen atoms. After isotropic least-squares refinement, all H atoms were inserted in chemically reasonable positions. Refinement continued anisotropically (H atoms isotropically), yielding $R = 0.074$, $R_w = 0.067$ for 1034 reflections; the 510 weak reflections were excluded.

Treatment of weak reflections

Exclusion from least-squares calculations of weak or unobserved reflections measured on diffractometers has been discussed by many authors. Stout & Jensen (1968) assert 'that rigorous analysis of the problem shows that there is no theoretical basis for dropping reflections and that the best results will be obtained from the complete data'. Hirshfeld & Rabinovich (1973), using a hypothetical model, demonstrated that rejection of weak reflections in least-squares refinement has only a cosmetic virtue as it produces smaller discrepancy indices; results that approach more closely to the 'true values' are those obtained including all reflections in the refinement.

In order to study the behaviour of the least-squares refinement with different modes for treating weak reflections, we have applied four different schemes of refinement of the final parameters. The treatment of weak reflections was similar to that used by Hirshfeld & Rabinovich (1973) in their theoretical approach. The quantity minimized in the least-squares full-matrix program was $\Delta = \sum w(k^2 F_o^2 - F_c^2)^2$. The results are summarized in Table 1.

The most important conclusion of the experiment is that, in contrast to the hypothetical model of Hirshfeld & Rabinovich (1973), the refined parameters are *not* affected by the different treatment of the weak reflections, as the differences in the parameters are smaller than their e.s.d.'s and the variations are not systematic. Exclusion of weak reflections affects significantly only R, which decreases from 0.17 in (d) $(n = 1544)$ to 0.04 in (c) $(n = 766)$. The variation in R_w is much smaller: from 0.075 in (d) to 0.059 in (c). The d

values, as well as the e.s.d.'s, increase, but not appreciably, with decreasing n. However, Derissen & Smit (1974) found significant differences in bond lengths, particularly O—H, when using different refinement schemes.

The experiment also confirms the relative inadequacy of R as an indicator of the accuracy of the structure (Stout & Jensen, 1968) and shows that R_w is better since the variation of R_w with n is considerably smaller than that of R.

Since the type of treatment of the weak reflections does not affect the structurally interesting parameters, the results which will be used are those obtained from scheme (b), in order to be consistent with the other structures analysed by us.*

Validity of the space group

The statistical tests for centrosymmetry mentioned above are not necessarily decisive in the present case in which the atomic distribution in the molecule shows pseudosymmetry $(mm2)$ and is not random. As the temperature factor U^{22} of C(9) is abnormally high $(0.167$ Å$^2)$ and there are some significant differences between chemically equivalent bond lengths and angles, we have considered the possibility that the space group is noncentrosymmetric.

Refinement of the finally determined centrosymmetric parameters by full-matrix least squares in $Pn2_1a$ led to $R = 0.063$ and $R_w = 0.058$ with scheme (a) (1034 reflections). 200 parameters were refined in comparison with 118 in $Pnma$.

In order to examine whether the drop in R_w is significant, the weighted residual test of Hamilton (1965) was applied.

In Hamilton's notation we have $\mathscr{R}_{200-118,\ 1034-200,\ \alpha}$, i.e. $\mathscr{R}_{82,834,\ \alpha}$, for the significance test. From his tables, for $\alpha = 0.005$, i.e. the $\frac{1}{2}\%$ significance level (the highest significance level given), $\mathscr{R} = 1.066$. The experimental ratio is 1.14 which appears to mean that there is considerably less than one chance in 200 that the centrosymmetric space group is correct.

However, the molecule thus refined is distorted, the differences between chemically equivalent bond lengths in the adamantane ring reaching 0.13 Å, while in the centrosymmetric structure the maximum difference is 0.02 Å. The e.s.d.'s and respective shifts for U^{12} and U^{23} are very large; the values for the other thermal parameters including U^{22} of C(9) are nearly equal to those obtained for the centrosymmetric space group.

Table 1. *Comparison of four refinement schemes differing in the treatment of weak reflections, applied to the same experimental data*

Scheme (a) omitted from refinement: reflections with $F_o^2 < \sigma(F_o^2)$.
Scheme (b) omitted from refinement: reflections with $F_o^2 < \sigma(F_o^2)$ only if $F_c < k\sigma(F_o^2)$.
Scheme (c) omitted from refinement: reflections with $F_o^2 < \sqrt{6}\sigma(F_o^2)$ [where 6 is the highest value of $F_o^4/\sigma(F_o^2)^2$ for symmetry-equivalent reflections having a negative value for at least one of the $I(hkl)$].
Scheme (d) accepted all the 1544 independent reflections.

	(a)	(b)	(c)	(d)
n	1034	1098	766	1544
R	0.074	0.077	0.044	0.170
R_w	0.066	0.067	0.059	0.075
d	1.37	1.34	1.46	1.21
k	0.5834	0.5832	0.5833	0.5829
$\sigma(k)$	0.0012	0.0012	0.0013	0.0011

n = number of reflections included in the last cycle.
$R = \sum|kF_o - |F_c||/\sum kF_o$; $\Delta = \sum w(k^2 F_o^2 - F_c^2)^2$.
$R_w = (\Delta/\sum wk^4 F_o^4)^{1/2}$.
$d = [\Delta/(n-s)]^{1/2}$; s = number of refined parameters = 118.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33414 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

In spite of the results of Hamilton's $\mathcal{R}$ test, the better consistency of equivalent bond lengths and angles and the magnitude of some of the e.s.d.'s suggests that the centrosymmetric structure is correct.

A similar experience has also been reported with other compounds, *e.g.* chromium hexacarbonyl (Whitaker & Jeffery, 1967) and 2,7-dichlorodibenzo-[1,4]dioxin (Boer & North, 1972) where better agreement in bond distances and angles prevails over the Hamilton $\mathcal{R}$ test.

The discussion is based on the centrosymmetric structure.

Table 2. *Fractional atomic coordinates* ($\times 10^5$ *for* C, O *and* Cl; $\times 10^3$ *for* H) *and their e.s.d.'s* [*calculated according to scheme* (*b*)]

	x	y	z
Cl(1)	32092 (6)	25000	−11099 (8)
O(1)	19675 (16)	25000	4325 (21)
C(4)	27501 (25)	25000	3433 (28)
C(1)	34476 (20)	25000	12975 (25)
C(2)	29478 (23)	25000	24579 (29)
C(3)	36253 (21)	25000	34592 (27)
C(5)	31086 (25)	25000	45908 (28)
O(2)	23305 (17)	25000	47021 (20)
Cl(2)	37815 (7)	25000	58758 (8)
C(9)	52878 (30)	25000	21339 (39)
C(6)	40277 (17)	6396 (48)	12170 (20)
C(7)	47029 (17)	6820 (57)	22133 (21)
C(8)	42154 (17)	6613 (50)	33806 (21)
H(3)	257 (1)	133 (3)	254 (2)
H(91)	569 (2)	250	271 (3)
H(92)	557 (2)	250	139 (3)
H(61)	433 (1)	71 (3)	47 (2)
H(62)	362 (1)	−55 (4)	127 (2)
H(7)	507 (2)	−54 (4)	216 (2)
H(81)	466 (1)	75 (4)	401 (2)
H(82)	386 (1)	−50 (4)	348 (2)

Results and discussion

Table 2 lists the atomic parameters. The e.s.d.'s in the positional parameters are nearly isotropic and average 0·001 for Cl, 0·003 for C and O and 0·02 Å for H.

Molecular shape

Fig. 1 shows a stereoview of the molecule [Figs. 1–4 were drawn by *ORTEP* (Johnson, 1971)]. C(1), C(2), C(3), C(9), H(91), H(92), and the two carbonyl chloride groups lie on the crystallographic mirror plane. The plane defined by C(6), C(7), C(8) is nearly parallel to this mirror plane. The conformation of the C–C–C=O group is synplanar, as is generally observed in saturated carboxylic acids (Dunitz & Strickler, 1968; Leiserowitz, 1976).

Bond lengths and angles

The bond lengths and angles for non-hydrogen atoms are shown in Fig. 2. Those involving H atoms are in Table 3.
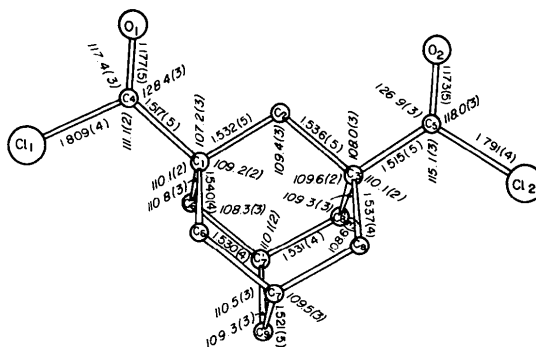

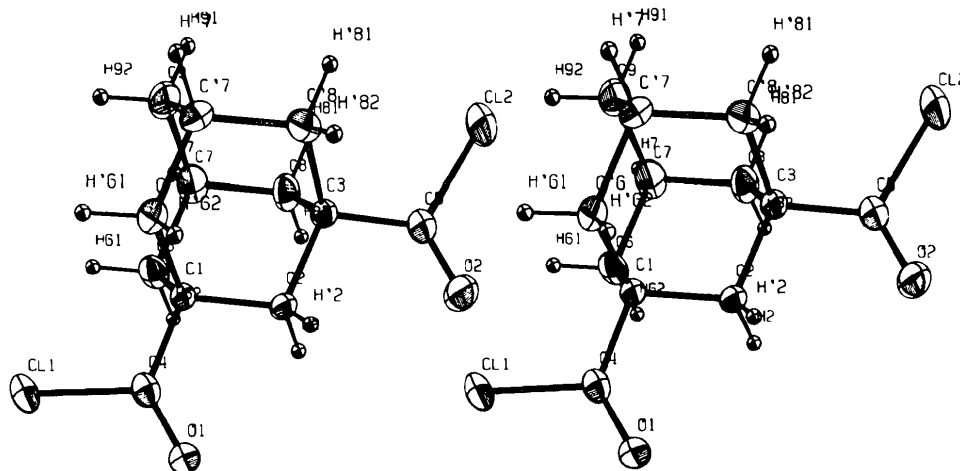Fig. 2. Bond lengths (Å) and angles (°) and their e.s.d.'s.

Fig. 1. Stereoscopic view of the molecule.

The r.m.s. values of the e.s.d.'s in the C—C lengths (0·004 Å) agree very well with that obtained from the bond scatter $\{[\sum (r_i - \bar{r})^2/(n - 1)]^{1/2} = 0\cdot004$ Å$\}$ of the adamantane-skeleton C—C bonds [excluding C(7)—C(9)] which average 1·534 Å. This value and the mean value (109·4°) of the bond angles agree well with the corresponding values in some other related compounds (Table 4). The skeleton of adamantane is quite rigid and its geometry is not affected by substitution and crystal packing forces.

The average length (1·516 Å) of C(1)—C(4) and C(3)—C(5) agrees well with those values of $C(sp^3)$ bonded to carbonyl $C(sp^2)$ found, for example, in bicyclo[2.2.2]octane-1,4-dicarboxylic acid (1·518 Å) (Ermer & Dunitz, 1969), acetone (1·515 Å) (Swalen & Costain, 1959) and 2-aminoadamantane-2-carboxylic acid hydrobromide (1·522 Å) (Chacko & Zand, 1973).

The two C—Cl bonds (1·791 and 1·809 Å) are significantly longer than those observed in the other three acyl chlorides analysed previously (1·769, 1·772 and 1·771 Å). This lengthening may be explained by the change in hybridization of the C atom which is attached here to a $C(sp^3)$ atom that is less electronegative than a $C(sp^2)$: according to Dewar & Schmeising (1960) the C—Cl length increases with decreasing s character of the C atom and the s character decreases with decreasing electronegativity of the substituent (Brockway, 1954; Bent, 1960).

Similarly, the C—Cl bond in phosgene, where the substituent is Cl, is 0·04 Å shorter than in acetyl chloride where the substituent is CH_3 (Simonetta & Beltrame, 1972).

C(4)—Cl(1) is 0·018 Å longer than the chemically equivalent C(5)—Cl(2). This difference, which is more than four times the e.s.d., is probably significant. The effect of curvilinear thermal motion cannot account for this difference. However, the two Cl atoms are involved in a short intermolecular C—Cl(1)···Cl(2)—C interaction which is possibly responsible for the lengthening of C(4)—Cl(1), as is discussed below.

Packing arrangement

A stereoscopic view of the packing along [100] is shown in Fig. 3. Fig. 4 shows the packing projected down [010]. Molecules (I), (II) and (III) lie on the mirror plane $y = \frac{1}{4}$ and molecules (IV), (V), (VI) and (VII) at $y = \frac{3}{4}$. No short Cl···O interactions are present. The shortest contacts between molecules related by the **b** translation are H···H of 2·67, 2·73 and 2·66 Å. The C···O contacts of 3·49 and 3·55 Å (Table 5), though longer than the 3·26 Å in muconyl chloride, may also be attributed to antiparallel $C^+=O^-$ dipole–dipole interactions. There is a short Cl···Cl contact (3·58 Å) that is accompanied by C—Cl··· Cl—C angles of 172 and 122°.

Table 3. *Bond lengths* (Å) *and angles* (°) *involving* H *atoms with their e.s.d.'s*

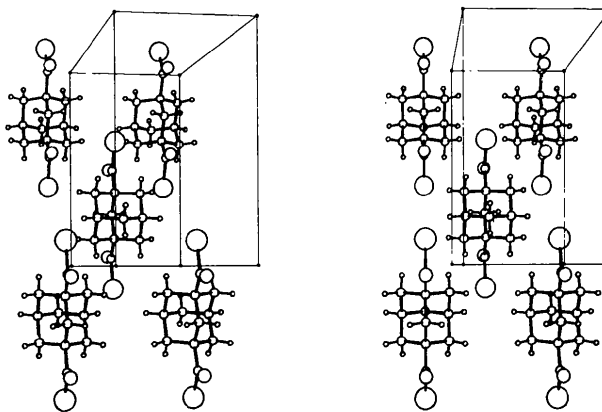| C(2)—H(2)	0·98 (2)	C(8)—H(81)	0·99 (2)
C(6)—H(61)	1·01 (3)	C(8)—H(82)	0·96 (2)
C(6)—H(62)	1·00 (3)	C(9)—H(91)	0·96 (3)
C(7)—H(7)	1·00 (2)	C(9)—H(92)	1·00 (3)
C(1)—C(2)—H(2)	111 (1)	C(9)—C(7)—H(7)	111 (1)
C(3)—C(2)—H(2)	108 (1)	C(3)—C(8)—H(81)	107 (1)
H(2)—C(2)—H(2')	108 (2)	C(3)—C(8)—H(82)	110 (1)
C(1)—C(6)—H(61)	106 (1)	C(7)—C(8)—H(81)	109 (1)
C(1)—C(6)—H(62)	108 (1)	C(7)—C(8)—H(82)	112 (1)
C(7)—C(6)—H(61)	111 (1)	H(81)—C(8)—H(82)	110 (2)
C(7)—C(6)—H(62)	111 (1)	C(7)—C(9)—H(91)	110 (1)
H(61)—C(6)—H(62)	112 (2)	C(7)—C(9)—H(92)	108 (1)
C(6)—C(7)—H(7)	108 (1)	H(91)—C(9)—H(92)	111 (3)
C(8)—C(7)—H(7)	108 (1)		

Fig. 3. Stereoscopic view of the packing along |100|.

Table 4. *Bond lengths* (Å) *and angles* (°) *in some adamantane derivatives*

Reference	1†	2	3	4	5	6‡
Bond length*	1·532 (6) Å	1·536 (5)	1·535 (7)	1·538 (19)	1·524 (12)	1·537
Bond angle*	109·5 (7)°	109·4 (6)	109·5 (13)	109·5 (8)	109·5 (14)	109·5

References: (1) ACl (present analysis); (2) adamantane (Donohue & Goodman, 1967); (3) biadamantane (Alden, Kraut & Traylor, 1968); (4) 2-aminoadamantane-2-carboxylic acid hydrobromide (Chacko & Zand, 1973); (5) 2-iodoadamantane (Wahl, Greene & Bordner, 1973); (6) adamantane (Gleicher & Schleyer, 1967).

* In parentheses: bond and angle scatter.
† All bonds included.
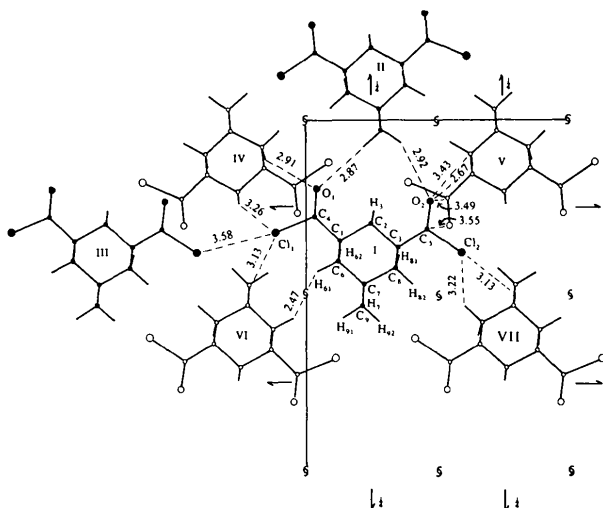‡ Theoretical treatment based on minimum-energy calculations.

Fig. 4. Packing along [010].

Table 5. *Short intermolecular contacts* (Å)

O(1)···H(91)^{II}	2·87	Cl(1)···H(7')^{VI}	3·13
C(2)···H(91)^{II}	3·38	C(6)···H(61')^{VI}	3·26
O(2)···H(92)^{II}	2·92	H(61)···H(61')^{VI}	2·47
Cl(1)···Cl(2)^{III}	3·58	Cl(2)···C(7)^{VII}	3·84
Cl(1)···H(2')^{IV}	3·26	Cl(2)···C(8)^{VII}	3·79
O(1)···C(5)^{IV}	3·55	Cl(2)···H(7)^{VII}	3·13
O(1)···H(82')^{IV}	2·91	Cl(2)···H(81)^{VII}	3·22
C(4)···C(5)^{IV}	3·75	H(81)···H(81')^{VII}	2·70
C(4)···O(2)^{IV}	3·49	H(62)···H(62)^{VIII}	2·66
O(2)···C(6)^{V}	3·43	H(7)···H(7)^{VIII}	2·67
O(2)···H(62')^{V}	2·66	H(82)···H(82)^{VIII}	2·73

Roman numeral superscripts refer to the molecules in the following equivalent positions relative to the reference molecule at x,y,z.

(I)		x,	y,	z	(V)	$\frac{1}{2}-x$,	$-y$,	$\frac{1}{2}+z$
(II)	$-\frac{1}{2}+x$,	y,	$\frac{1}{2}-z$		(VI)	$1-x$,	$-y$,	$-z$
(III)		x,	y,	$-1+z$	(VII)	$1-x$,	$-y$,	$1-z$
(IV)	$\frac{1}{2}-x$,	$1-y$,	$-\frac{1}{2}-z$		(VIII)	x,	$-\frac{1}{2}-y$,	z

βICl αICl
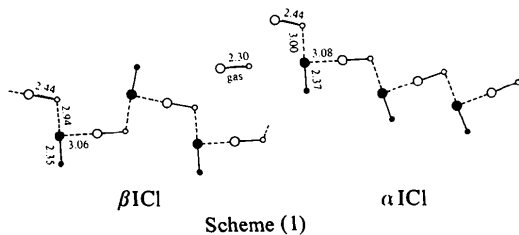
Scheme (1)

Sakurai, Sundaralingam & Jeffrey (1963) recognized, from the examination of a series of Cl-containing compounds where short C—Cl···Cl—C contacts occur, that there is an orientation factor associated with these short contacts: either the two bonds are nearly collinear (C—Cl···Cl—C angles of 160 ± 10°), or the two bonds are nearly perpendicular (C—Cl···Cl—C angles of 175 and 80°).

The second type of geometry is similar to that found in molecular I_2, Br_2 and Cl_2 and in the α and β forms of

ICl (Boswijk, van der Heide, Vos & Wiebenga, 1956; Carpenter & Richards, 1962).

The packing arrangements of the latter [scheme (1)], recognized by Bent (1968) as an electron-pair donor–acceptor interaction of the Hassel type (parts I and VII) where the same atoms may act as donor or acceptor, depending on the orientation, is of considerable interest in our context.

As may be seen from scheme (1) there are two distinct types of molecules as far as the I—Cl length is concerned (2·44 Å in α and β forms; 2·37, 2·35 Å in α and β respectively). In the first type the I atom (large, open circles) acts as an acceptor only, while in the second type (large, filled circles) it acts as a donor for the first-type I atom and as an acceptor for the Cl.

The Cl···Cl contacts in adamantane-1,3-dicarbonyl chloride (C—Cl···Cl—C angles of 172 and 122°) resemble this geometry, the bond adjacent to the acceptor Cl(1) being longer than that of the donor Cl(2).
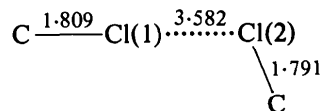
Scheme (2)

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Molecular Packing Modes of Acyl Halides.
VI. The Crystal and Molecular Structure of Terephthaloyl Bromide

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The structure of terephthaloyl bromide (TBr) has been refined to $R = 0.059$, $R_w = 0.14$. Crystals are monoclinic, space group $P2_1/c$, with $a = 4.0632$ (4), $b = 10.9096$ (4), $c = 10.2214$ (6) Å, $\beta = 96.43$ (1)°, $Z = 2$. The molecules are nearly planar, the carbonyl bromide group being rotated only $7.7°$ from the phenyl ring. The molecular structure (excluding the C–Br bond) is essentially identical to that of TCl, the only exception being the exocyclic C–C bond which is 0.02 Å longer in the present case. Bond lengths of the CCOBr group are: C–C 1.502, C=O 1.181, C–Br 1.931 Å. Short intermolecular Br$\cdots$O contacts are not observed; there is a short Br$\cdots$Br contact of 3.57 Å, accompanied by a C–Br$\cdots$Br angle of 159°. The shortest H$\cdots$O contact is 2.54 Å.

Introduction

Amongst the four acyl chloride structures analysed thus far, the only one that exhibited a hal$\cdots$O interaction similar to that found in oxalyl bromide was TCl.

Since hal$\cdots$O interactions are stronger for Br than for Cl (Bent, 1968), it was expected that replacement of Cl by Br in a structure having a Cl$\cdots$O interaction would result either in an isomorphous structure or at least in one showing Br$\cdots$O interactions.

The space group of TBr is the same as that of TCl; however, the cell constants are different. In order to determine whether the packing modes are similar in both compounds, the structure analysis of TBr was undertaken.

Experimental

Crystals of TBr grown by sublimation are colourless monoclinic plates showing the {012}, {021} and {10$\bar{1}$} forms.

Cell constants were determined by least squares from 13 medium- and high-order reflections ($57 < \theta < 70°$) measured on a Siemens diffractometer with Cu $K\alpha$ radiation.

Crystal data

Terephthaloyl bromide, $C_8H_4Br_2O_2$, $M_r = 291.93$, m.p. 84°C, monoclinic, $a = 4.0632$ (4), $b = 10.9096$ (4), $c = 10.2214$ (6) Å, $\beta = 96.43$ (1)°, $U = 450.25$ Å^3, $Z = 2$, $D_c = 2.154$ g cm^{-3}, $F(000) = 276$, μ(Cu $K\bar{\alpha}$) = 121.7 cm^{-1}, space group $P2_1/c$.

A crystal, $0.11 \times 0.24 \times 0.33$ mm measured normal to the faces (021), (0$\bar{1}$2) and (10$\bar{1}$), was mounted along a^* on an automatic Siemens diffractometer controlled by an IBM 1800 computer. 1834 reflections (sin $\theta/\lambda < 0.61$ Å^{-1}) were recorded with Cu $K\alpha$ radiation filtered by Ni foil and the ω–2θ scan technique. Scan ranges varied from 0.57 to 1.1° in θ. The background was measured over the same range with an ω offset of 0.6°; time of measurement was 0.2 s per 0.01° step interval